

# Supporting Information

## Acceptorless Dehydrogenative Coupling using Ammonia: Direct Synthesis of N-Heteroaromatics from Diols Catalyzed by Ruthenium

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## 1. General Procedure

All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques under argon atmosphere. All solvents were reagent grade or better. Non-deuterated solvents were dried over sodium/benzophenoneketyl (tetrahydrofuran, n-pentane, and toluene), and distilled under argon atmosphere. All solvents were degassed with argon and kept in the glove box over activated 4Å molecular sieves. Deuterated solvents were purchased from Aldrich, purged with argon and stored over activated 4Å molecular sieves in the glove box.  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectra were recorded using Bruker AMX-300, 400 and 500 NMR spectrometer. All spectra were recorded at 298 K, unless otherwise noted.  $^1\text{H}$  NMR and  $^{13}\text{C}\{^1\text{H}\}$  NMR chemical shifts are reported in ppm downfield from tetramethylsilane and referenced to the residual signals of an appropriate deuterated solvent.  $^{31}\text{P}\{^1\text{H}\}$  NMR chemical shifts are reported in ppm downfield from  $\text{H}_3\text{PO}_4$  and referenced to an external 85% solution of phosphoric acid in  $\text{D}_2\text{O}$ . NMR spectroscopy abbreviations: br, broad; s, singlet; d, doublet; m, multiplet. GCMS was carried out on HP 6890 (flame ionization detector and thermal conductivity detector) and HP 5973 (MS detector) instruments equipped with a 30 m column (Restek 5MS, 0.32 mm internal diameter) with a 5% phenylmethylsilicone coating (0.25 mm) and helium as carrier gas. Most of the commercially available reagents were used as received.

Ligand  $\text{Acr-CH}_2\text{PNP}^{\text{iPr}}$  and the ruthenium complexes **1**, **2** were prepared according to literature procedures.<sup>1,2</sup>

## 2. Experimental

### a) General procedure for the pyrazine formation reaction:

**For Table 1:** To a solution of 0.01 mmol catalyst **1** in 2 mL dry toluene in a 100 ml Fisher Porter tube was added 1 mmol of 1,2-diol substrate under  $\text{N}_2$  atmosphere. The tube was closed and was taken out from the box and purged with 2 bar of ammonia for 3 times and finally pressurized with 7 bar of ammonia. The reaction mixture was stirred at  $150^\circ\text{C}$  for 36h, cooled down to room temperature and the ammonia pressure was released in the

hood. The reaction products were analyzed by GC-MS and  $^1\text{H}$  NMR, and the pyrazines were isolated after column chromatography.

**Table S1. Pyrazine formation from 1,2-diols and ammonia<sup>a</sup>**

Entry	Substrate	Products	Mass	R.T.	Yield <sup>b</sup> [A/B]
1			192	14.31 14.58	99 [65/35]
2			304	19.84 20.19	99 [50/50]
3			416	25.91 27.14	99 [58/42]
4			232	20.02 20.34	100 [68/32]
5 <sup>c</sup>			136	10.75	72
6 <sup>c</sup>			108	8.28	42
7 <sup>c</sup>			136	10.73	85 (15) <sup>d</sup>
8			188	16.51	95 (5) <sup>d</sup>

<sup>a</sup>Reaction conditions: Catalyst **1** (0.01 mmol), 1,2-diol (1 mmol), 150°C, 36h, toluene (2ml), <sup>b</sup>Isolated yield. <sup>c</sup>GC-MS yield with mesitylene as internal standard. <sup>d</sup>hydrogenated product. R.T.= Retention Time

**b) General procedure for the N-substituted pyrrole formation reaction (for Table S2):** To a solution of 0.01 mmol catalyst **1** in 0.5 mL (or 2 mL for entry 1, 2) of dry toluene in a 100 ml Fisher Porter tube was added the specified amounts of 2,5-hexanediol and 1-hexanol under N<sub>2</sub> atmosphere. The tube was closed and was taken out from the box and purged with 2 bar of ammonia 3 times and finally pressurized with 7 bar of ammonia.

The reaction mixture was stirred at 150°C for 24h, cooled down to room temperature and the ammonia pressure was released in the hood. The reaction products were analyzed by GC-MS and <sup>1</sup>H NMR to determine the yield with mesitylene as internal standard.

**Table S2. Optimization of pyrrole formation from alcohols and ammonia <sup>a</sup>**

Reaction scheme: 2,5-hexanediol + 1-hexanol  $\xrightarrow[\text{Tol. 150}^\circ\text{C, 24h}]{[\text{Ru}] / \text{NH}_3}$  A + B + C

Entry	[Ru] (mol%)	Toluene (mL)	2,5-Hexanediol (mmol)	1-Hexanol (mmol)	Yield (%)		
					A	B	C
1	<b>1</b> (2)	2	0.5	0.5	17	18	35
2	<b>1</b> (2)	2	0.5	1	42	8	46
3	<b>1</b> (1)	0.5	1	1	63	11	24
<b>4</b>	<b>1</b> (1)	<b>0.5</b>	<b>1</b>	<b>2</b>	<b>90</b>	<b>8</b>	<b>2</b>
5	<b>1</b> (0.5)	0.5	1	1	74	4	19
6 <sup>c</sup>	<b>1</b> (1)	-	1	2	30	12	46
7 <sup>d</sup>	<b>2</b> (1)	0.5	1	2	50	12	32
8 <sup>e</sup>	<b>2</b> (1)	0.5	1	2	68	12	18

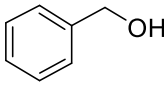
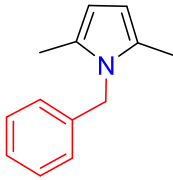
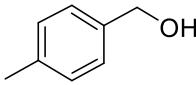
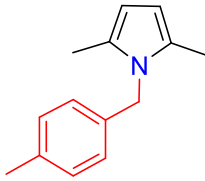
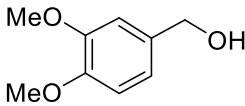
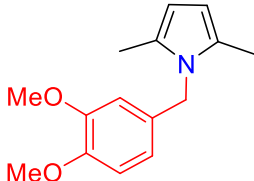
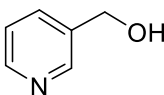
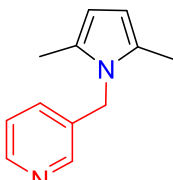
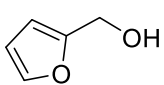
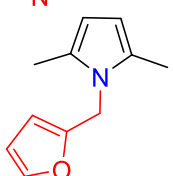
<sup>a</sup>Reaction conditions: Catalyst **1** (as mentioned), 2,5-hexanediol (as mentioned), 1-hexanol (as mentioned), ammonia (7 bar), 150°C, 24h, toluene (as mentioned), <sup>b</sup>GC-MS for detection and <sup>1</sup>H NMR for yield with mesitylene as internal standard. <sup>c</sup>neat condition, solvent free. <sup>d</sup>Catalyst **2** [Ru(H-AcrCH<sub>2</sub>PNP<sup>i</sup>Pr)H(CO)], (0.01 mmol). <sup>e</sup>Catalyst **2** [Ru(H-AcrCH<sub>2</sub>PNP<sup>i</sup>Pr)H(CO)], (0.01 mmol) and NH<sub>4</sub>Cl (2 mol%).

### For Table 3 and S3:

To a solution of 0.01 mmol catalyst **1** in 0.5 mL dry of toluene in a 100 ml Fisher Porter tube were added 1 mmol of 2,5-hexanediol and 2 mmol of primary alcohol (4 mmol for low boiling primary alcohols, Table S3, entries 8-10) under N<sub>2</sub> atmosphere. The tube was closed and was taken out from the box and purged with 2 bar of ammonia 3 times and finally pressurized with 7 bar of ammonia. The reaction mixture was stirred at 150°C for 24h, cooled down to room temperature and the ammonia pressure was released in the hood. The reaction products were analyzed by GC-MS and <sup>1</sup>H NMR to determine the yield with mesitylene as internal standard.

**Table S3. Pyrrole formation from alcohols and ammonia<sup>a</sup>**

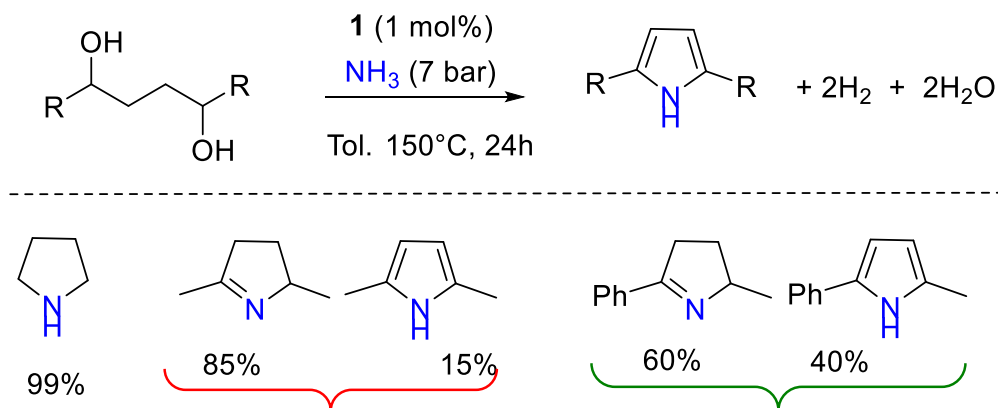
Entry	alcohol (mmol)	Product	Mass	Rt in GCMS	Yield (%)		
					A	B	C
1	<chem>CCCCCO</chem>		179	13.96	90	8	2
2	<chem>CCCCCO</chem>		207	15.61	83	7	9
3	<chem>CCCCO</chem>		165	13.06	76	11	10
4	<chem>CCCCO</chem>		151	12.14	77	13	10
5	<chem>CCNCCO</chem>		180	13.89	74	17	8
6	<chem>c1ccccc1CO</chem>		199	15.98	76	6	18
7	<chem>c1ccccc1CCO</chem>		213	17.11	74	5	20
8 <sup>c</sup>	<chem>CCO</chem>		137	11.06	74	19	5
9 <sup>c</sup>	<chem>CO</chem>		123	10.03	71	20	7
10 <sup>c</sup>	MeOH		109	9.50	29	10	55

11			185	15.04	57	4	36
12			199	15.91	48	8	45
13			245	18.11	13	-	-
14			186	15.88	69	12	14
15			175	13.59	84	9	5

<sup>a</sup>Reaction conditions: Catalyst **1** (0.01 mmol), 2,5-hexanediol (1 mmol), primary alcohol (2 mmol), ammonia (7 bar), 150°C, 24h, toluene (0.5 mL), <sup>b</sup>GC-MS for detection and <sup>1</sup>H NMR yield with mesitylene as internal standard. <sup>c</sup>Primary alcohol (4 mmol).

### 3. Treatment of 1,4-diol derivatives with catalyst **1** and ammonia with no added primary alcohol

To a solution of 0.01 mmol catalyst **1** in 2 mL dry of toluene in a 100 ml Fisher Porter tube was added 1 mmol of 1,4-diols under N<sub>2</sub> atmosphere. The tube was closed and was taken out from the box and purged with 2 bar of ammonia for 3 times and finally pressurized with 7 bar of ammonia. The reaction mixture was stirred at 150°C for 24h, cooled down to room temperature and the ammonia pressure was released in the hood. The reaction products were analyzed by GC-MS and <sup>1</sup>H NMR to determine the yield with mesitylene as internal standard. 1,4-butanediol used as substrate yielded pyrrolidine as the single product and 2,5-hexanediol afforded a mixture of 85% yield of 2,5-dimethyl-1-pyrroline and 15% yield of the 2,5-dimethylpyrrole. Use of 1-phenyl-1,4-pentanediol afforded 60% of 2-methyl-5-phenyl-1-pyrroline and 40% yield of the 2-methyl-5-phenylpyrrole.



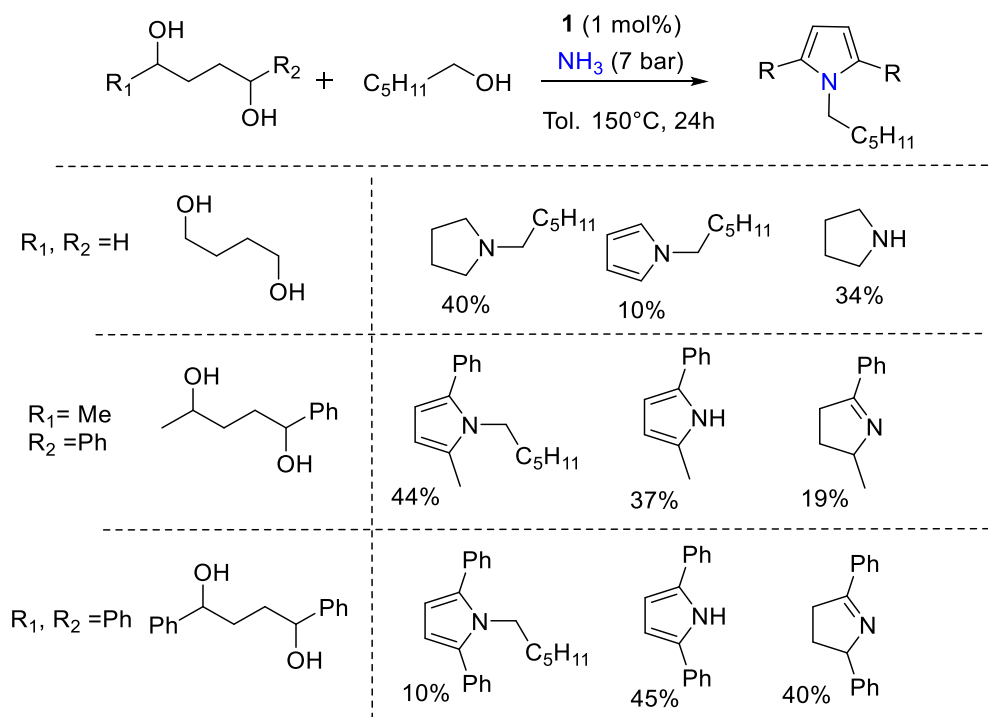
**Figure S1.** Reaction of 1,4-butanediol substrates with ammonia in presence of catalyst **1**

### 4. Treatment of other 1,4-diol derivatives and 1-hexanol with catalyst **1** and ammonia:

To a solution of 0.01 mmol catalyst **1** in 0.5 mL dry of toluene in a 100 ml Fisher Porter tube was added 1 mmol of 1,4-diols and 2 mmol of 1-hexanol under N<sub>2</sub> atmosphere. The tube was closed and was taken out from the box and purged with 2 bar of ammonia for 3

times and finally pressurized with 7 bar of ammonia. The reaction mixture was stirred at 150°C for 24h, cooled down to room temperature and the ammonia pressure was released in the hood. The reaction products were analyzed by GC-MS and  $^1\text{H}$  NMR to determine the yield with mesitylene as internal standard.

The treatment of 1,4-butanediol with 1-hexanol and ammonia N-hexylpyrrolidine as the coupling product (40%) along with N-hexylpyrrole (10%) and pyrrolidine was observed. Under the optimized conditions, reaction of 1-phenyl-1,4-pentanediol and 1-hexanol with ammonia afforded 44% yield of the 1-hexyl-2-phenyl-5-methyl pyrrole and 37% of the 2-phenyl-5-methyl pyrrole and 37% 2-methyl-5-phenyl-1-pyrroline was formed and 1-hexanol fully converted to 1-hexylamine and dihexylamine. 1-hexyl-2,5-diphenyl pyrrole was formed in 10% yield from the 1,4-diphenyl-1,4-butanediol and 1-hexanol with 2,5-diphenylpyrrole as the major product.

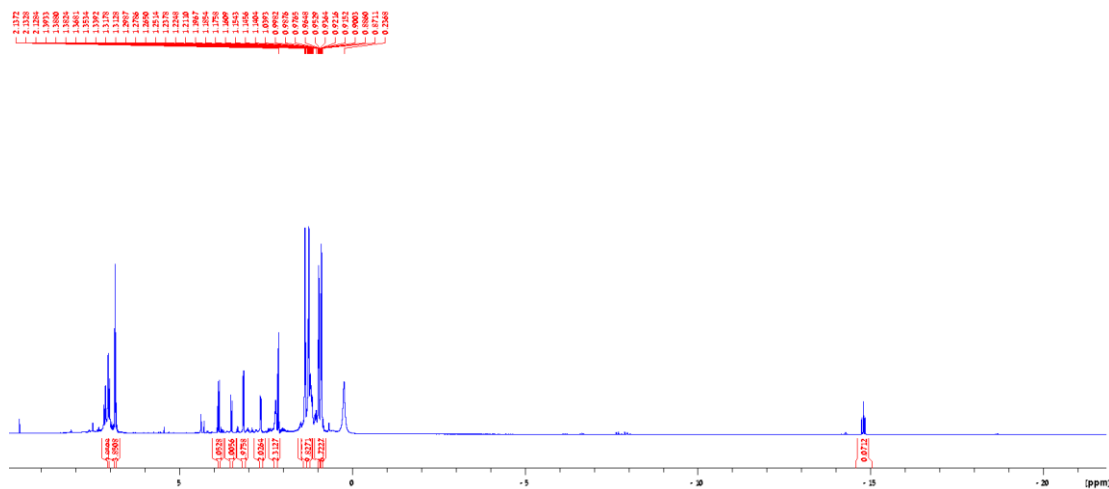


**Figure S2.** Reaction of 1,4-butanediol substrates and 1-hexanol with ammonia in presence of catalyst **1**

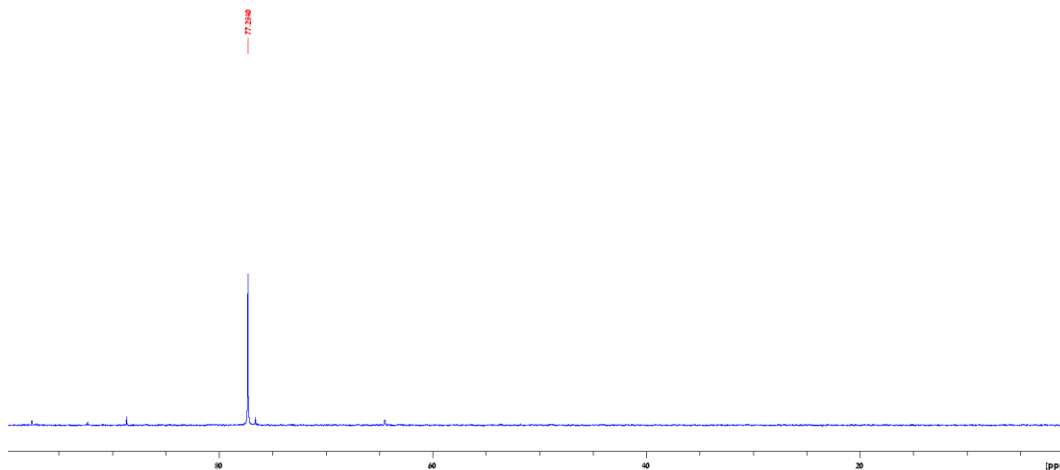


## 5. Synthesis of complex 3:

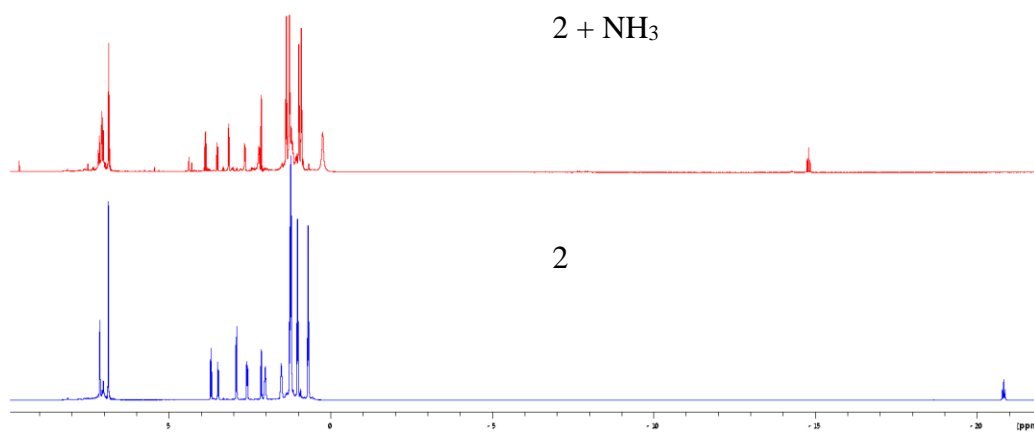
14 mg (0.02 mmol) of Ru(H-AcrCH<sub>2</sub>PNP<sup>i</sup>Pr)H(CO) (**2**) was taken in J Young NMR tube and dissolved in 0.5 mL d<sub>8</sub>-toluene under N<sub>2</sub> atmosphere. The gas was removed by freeze pump thaw and charged with 1 bar of NH<sub>3</sub>. An immediate change of the color from orange to light yellow took place, indicating that NH<sub>3</sub> was bounded to the Ru center. <sup>1</sup>H NMR (Tol-d<sub>8</sub>, 500 MHz): δ = -14.8 (t, *J*= 23.4Hz, 1H, Ru-H), 0.23 (br, 3H, NH<sub>3</sub>), 0.89 (m, 6H), 0.97 (m, 6H), 1.19 (m, 2H), 1.25 (m, 6H), 1.36 (m, 6H), 2.22 (m, 2H), 2.64 (m, 2H), 3.15 (d, *J*=12.1Hz, 2H), 3.49 (d, *J*=16.2Hz, 1H), 3.86 (d, *J*=16.5Hz, 1H), 6.84-6.87 (m, 3H), 7.06-7.08 (m, 3H). <sup>31</sup>P{<sup>1</sup>H} NMR (Tol-d<sub>8</sub>, 202 MHz): δ = 77.28



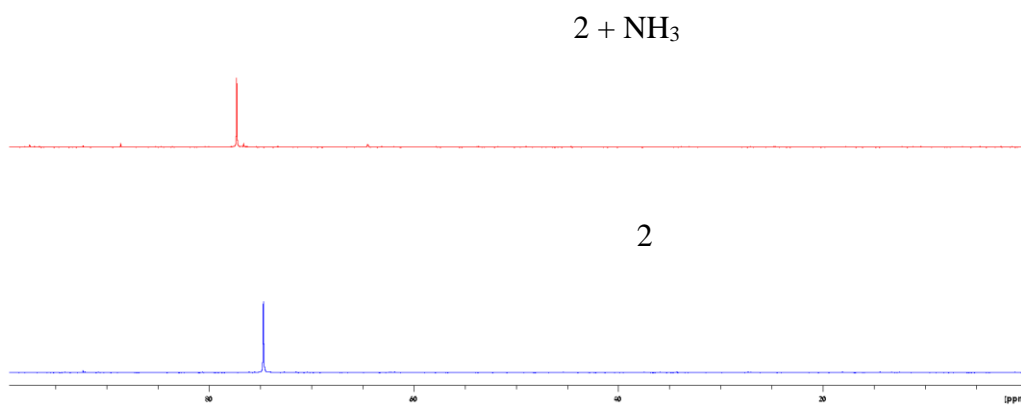
**Figure S3.** <sup>1</sup>H NMR spectrum of complex **3** in tol-d<sub>8</sub>



**Figure S4.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of complex **3** in tol-d<sub>8</sub>



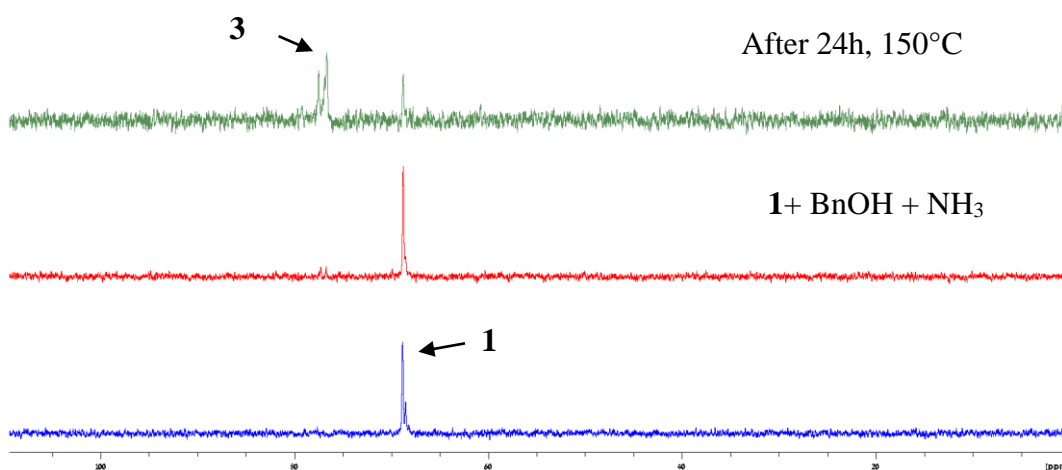
**Figure S5.**  $^1\text{H}$  NMR spectrum for the reaction of complex **2** and  $\text{NH}_3$  in  $\text{tol-d}_8$



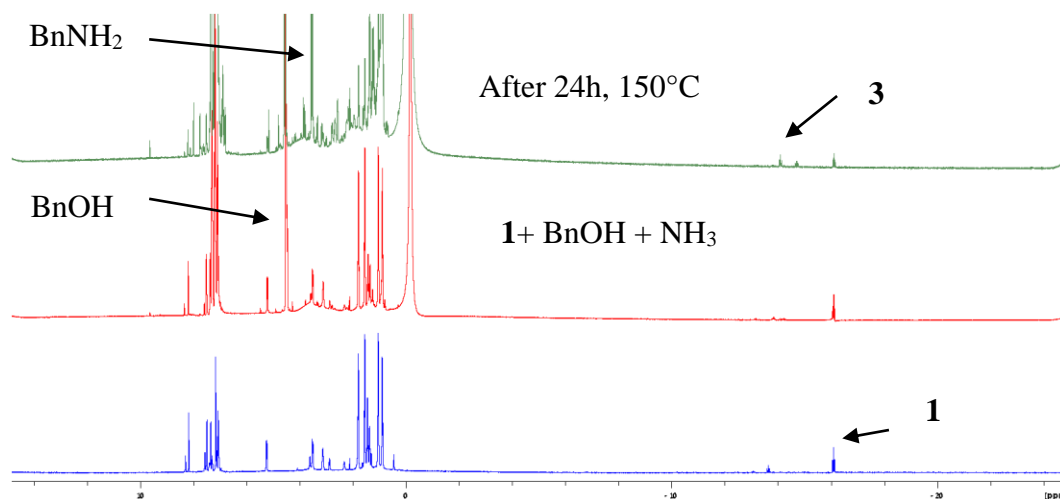
**Figure S6.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum for the reaction of complex **2** and  $\text{NH}_3$  in  $\text{tol-d}_8$

## 6. Reaction of complex **1** and benzyl alcohol in presence of ammonia:

7 mg (0.01 mmol) of  $\text{Ru}(\text{AcrCH}_2\text{PNP}^{\text{iPr}})\text{HCl}(\text{CO})$  (**1**) was placed in a high pressure NMR tube and dissolved in 0.5 mL  $\text{C}_6\text{D}_6$  under  $\text{N}_2$  atmosphere. 5 equivalent of benzyl alcohol was added to the NMR tube and it was taken out from the glove box and purged with 2 bar of ammonia 3 times and finally pressurized with 7 bar of ammonia. The NMR tube was heated at  $150^\circ\text{C}$  for 24h, forming benzyl amine. The formed ammonia-bound complex **3** was observed after the reaction by  $^{31}\text{P}$  NMR at 77.28 ppm and in  $^1\text{H}$  NMR the Ru-H appears at  $-14.8$  ppm.



**Figure S7.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum for the reaction of **1** and benzyl alcohol with  $\text{NH}_3$  in  $\text{C}_6\text{D}_6$

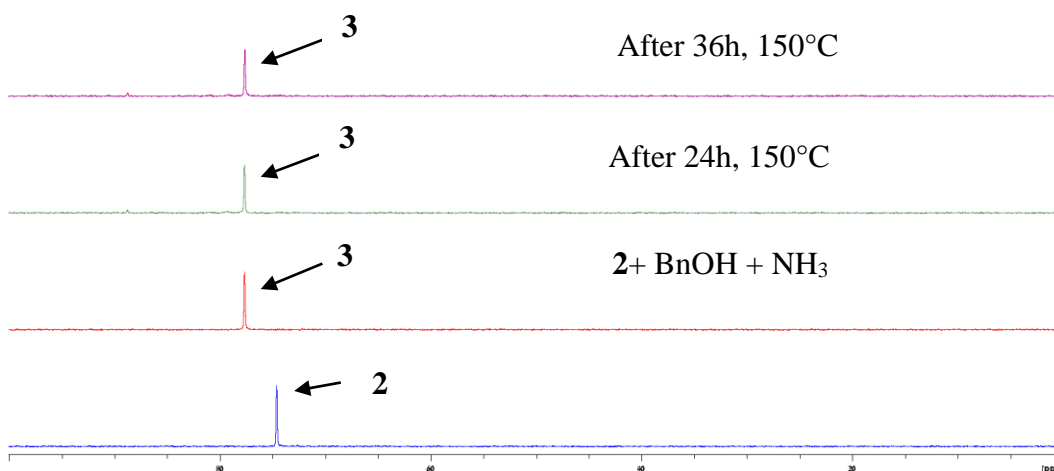


**Figure S8.**  $^1\text{H}$  NMR spectrum for the reaction of **1** and benzyl alcohol with  $\text{NH}_3$  in  $\text{C}_6\text{D}_6$

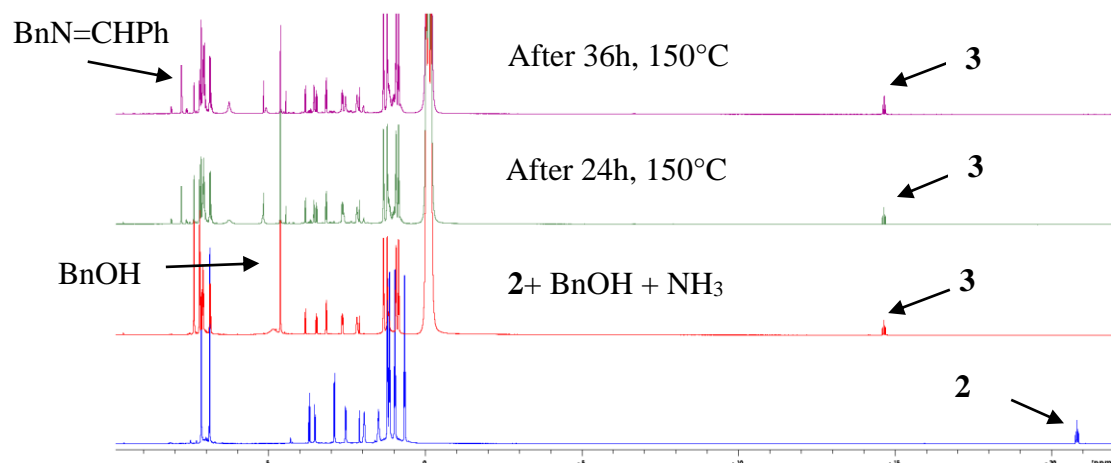
## 7. Reaction of complex **2** and benzyl alcohol in presence of ammonia:

To a solution of 7 mg (0.01 mmol) of  $\text{Ru}(\text{H-AcrCH}_2\text{PNP}^{\text{iPr}})\text{H}(\text{CO})$  (**2**) in 0.5 mL  $\text{C}_6\text{D}_6$  in a high pressure NMR tube under  $\text{N}_2$  were added 5 equivalents of benzyl alcohol. The reaction mixture was taken out of the glove box and purged with 2 bar of ammonia 3 times and finally pressurized with 7 bar of ammonia. Immediate formation of complex **3** was observed after addition of ammonia. The NMR tube was heated at  $150^\circ\text{C}$  for 24h. N-benzylidenebenzylamine formation was observed and the ammonia-bound complex **3** was still present.

Under the optimized condition (1 mmol of benzyl alcohol, 0.01 mmol of catalyst **2**, 2 ml toluene, 7 bar  $\text{NH}_3$ ,  $150^\circ\text{C}$ , 24h), full conversion of benzyl alcohol to benzyl amine (90%) and N-benzylidenebenzylamine (10%) was observed.

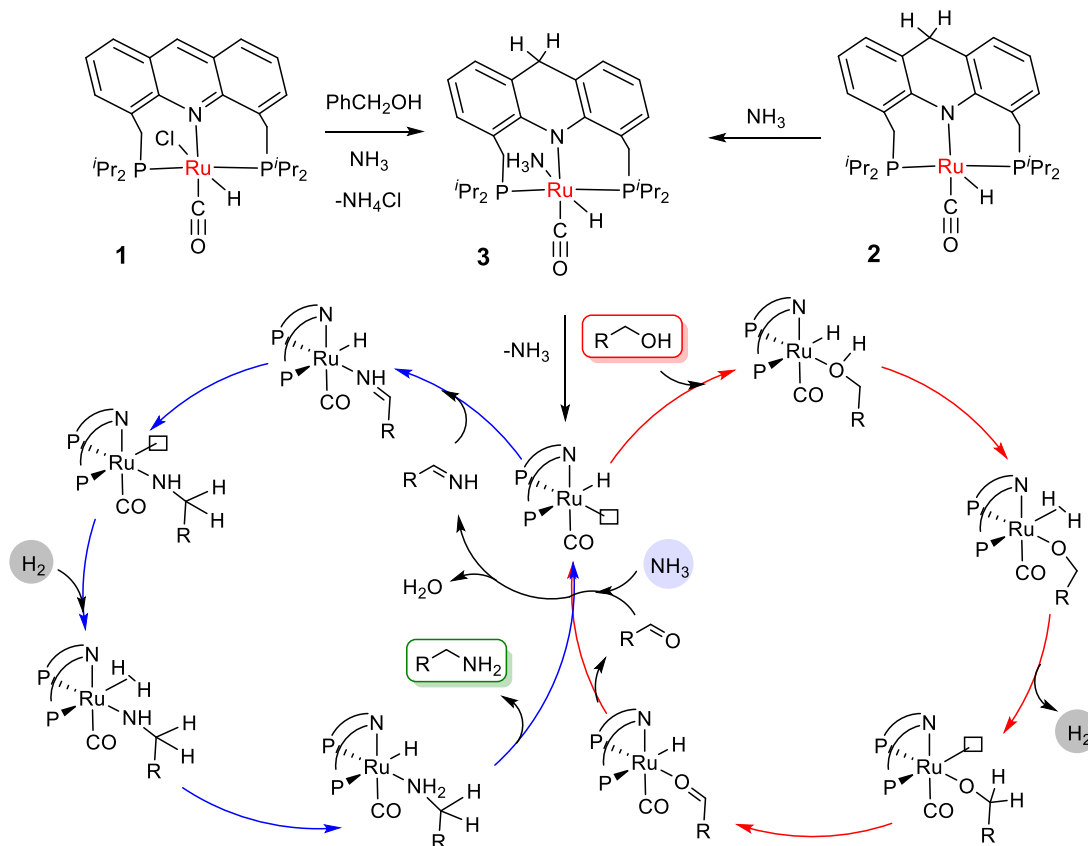


**Figure S9.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the reaction of **1** and benzyl alcohol with  $\text{NH}_3$  in  $\text{C}_6\text{D}_6$



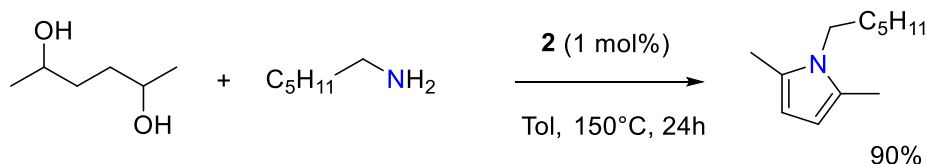
**Figure S10.**  $^1\text{H}$  NMR spectrum for the reaction of **2** and benzyl alcohol with  $\text{NH}_3$  in  $\text{C}_6\text{D}_6$

## 8. Proposed mechanism for alcohol amination



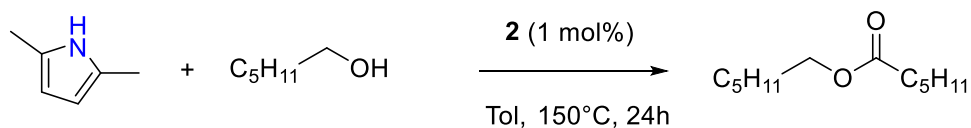
### 9. Reaction of 2,5-hexanediol and 1-hexylamine with complex 2

To a solution of 0.005 mmol catalyst **2** in 2 mL dry of toluene in a 50 ml Teflon Schlenk tube was added 0.5 mmol of 2,5-hexanediol and 0.5 mmol 1-hexylamine under N<sub>2</sub> atmosphere. The reaction mixture was stirred at 150°C for 24h, cooled down to room temperature and the formed hydrogen was released in the hood. The reaction products were analyzed by GC-MS with mesitylene as internal standard. N-hexyl-2,5-dimethylpyrrole was afforded with 90% yield.

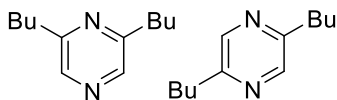


### 10. Reaction of 2,5-dimethylpyrrole and 1-hexanol with complex 2

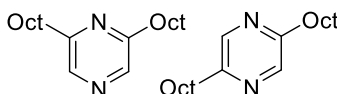
To a solution of 0.005 mmol catalyst **2** in 2 mL dry of toluene in a 50 ml Teflon Schlenk tube was added 0.5 mmol of 2,5-dimethylpyrrole and 0.5 mmol 1-hexanol under N<sub>2</sub> atmosphere. The reaction mixture was stirred at 150°C for 24h, cooled down to room temperature and the formed hydrogen was released in the hood. The reaction products were analyzed by GC-MS with mesitylene as internal standard. Hexyl hexanoate (72%) was observed as the major product with unreacted 2,5-dimethylpyrrole and N-hexyl-2,5-dimethylpyrrole was not formed.



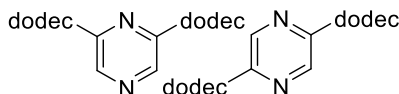
## 11. $^1\text{H}$ and $^{13}\text{C}$ NMR data of isolated pyrazines:



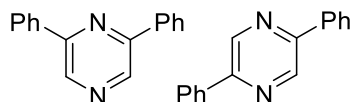
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.96 (t,  $J = 7.62\text{Hz}$ , 3H), 1.39-1.43 (m, 2H), 1.71-1.74 (m, 2H), 2.79 (t,  $J = 7.93\text{Hz}$ , 2H), 8.26, 8.32 (s, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 13.8, 13.8, 22.4, 22.4, 31.6, 31.8, 34.7, 35.3, 141.3, 143.3, 154.6, 156.8.



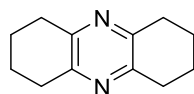
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.97 (t,  $J = 6.57\text{Hz}$ , 3H), 1.36-1.43 (m, 10H), 1.81-1.83 (m, 2H), 2.89 (t,  $J = 7.53\text{Hz}$ , 2H), 8.38, 8.47 (s, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 14.0, 22.6, 29.2, 29.2, 29.3, 29.3, 29.4, 29.5, 29.6, 31.8, 34.9, 35.4, 141.1, 143.0, 154.6, 156.8.



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.90 (t,  $J = 7.06\text{ Hz}$ , 3H), 1.27-1.33 (m, 18H), 1.74-1.78 (m, 2H), 2.85 (t,  $J = 7.57\text{Hz}$ , 2H), 8.33, 8.44 (s, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 14.1, 22.7, 29.2, 29.3, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 31.9, 142.4, 154.6.

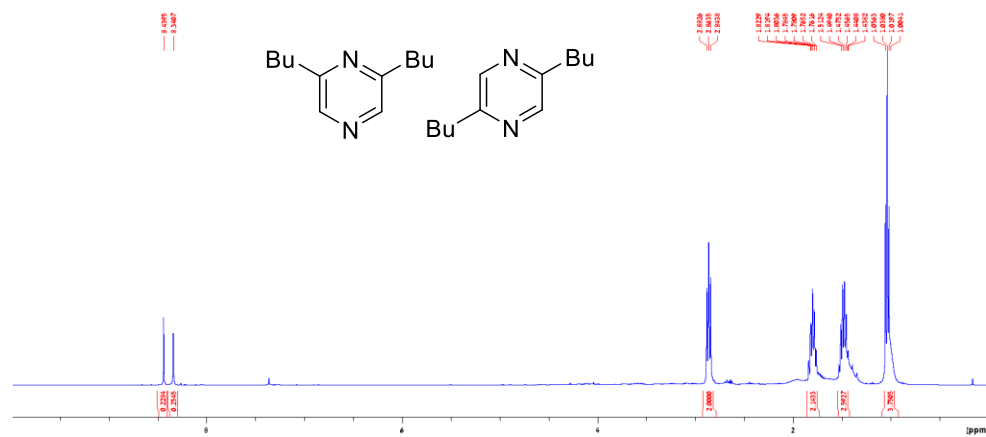


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.52-7.57 (m, 3H), 8.09 (d,  $J = 7.56\text{Hz}$ , 1H), 8.18 (d,  $J = 7.65\text{Hz}$ , 1H), 9.00, 9.01 (s, 1H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 126.8, 127.0, 128.9, 129.0, 129.1, 129.8, 130.0, 133.3, 141.2, 150.7.

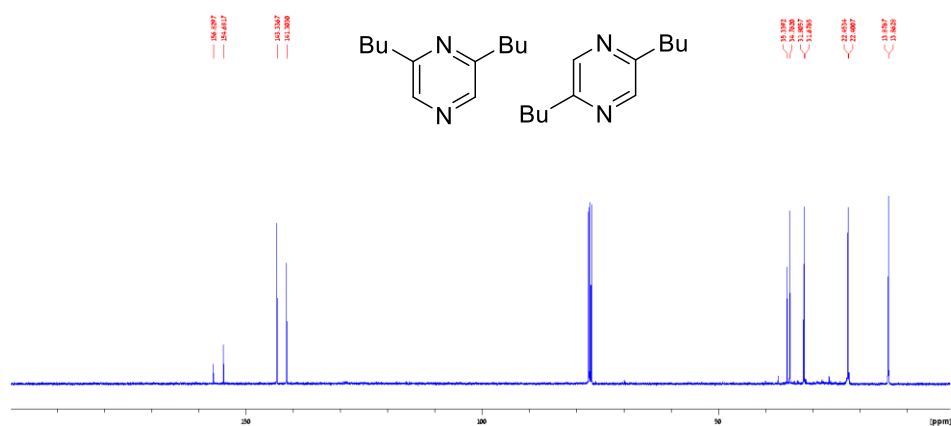


$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ : 1.92 (br, 2H), 2.93 (br, 2H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 22.5, 31.2, 149.3.

## 12. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of isolated pyrazines:

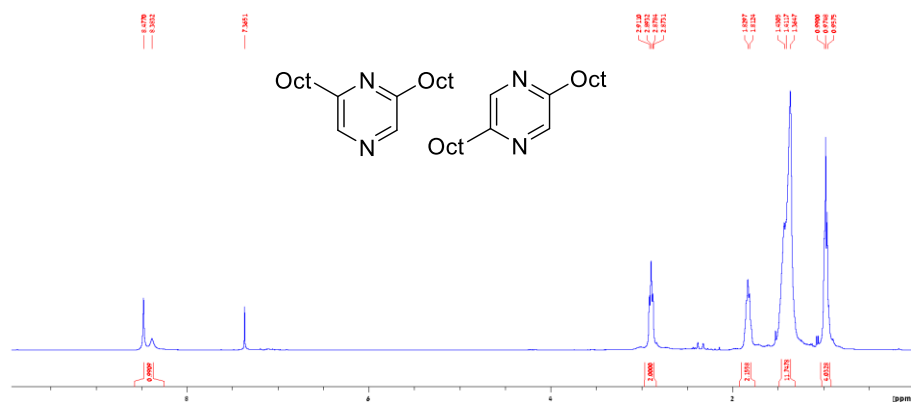


**Figure S11.**  $^1\text{H}$  NMR of dibutylpyrazine

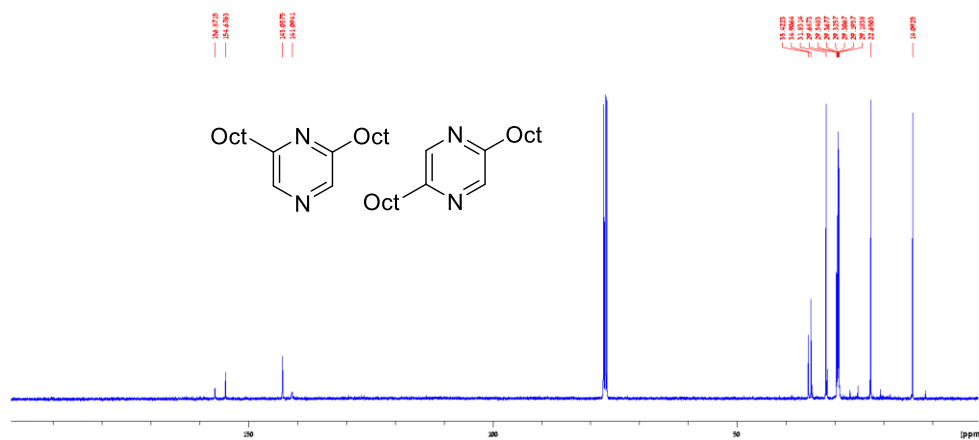


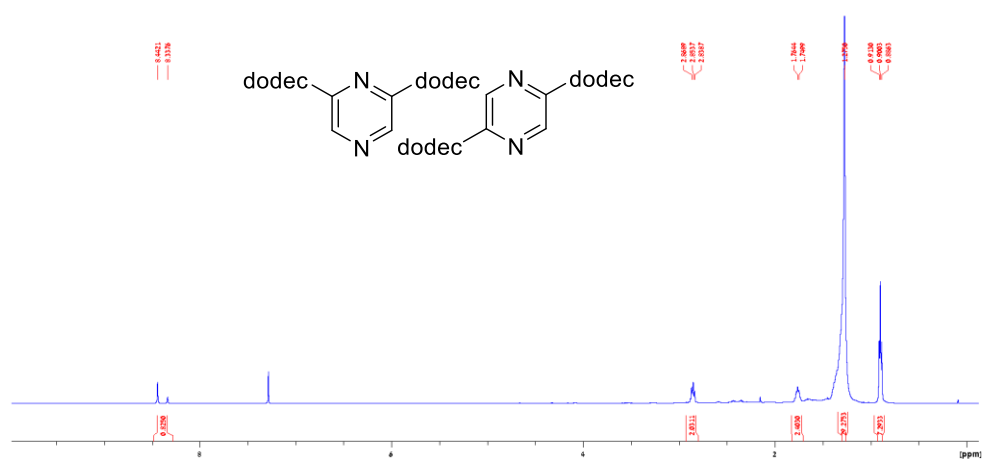
**Figure S12.**  $^{13}\text{C}\{^1\text{H}\}$  NMR of dibutylpyrazine



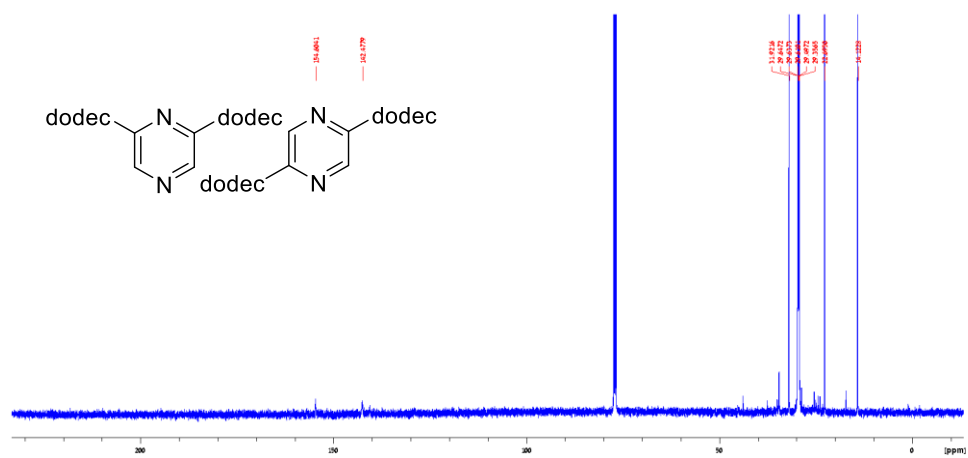


**Figure S13.** <sup>1</sup>H NMR of dioctylpyrazine

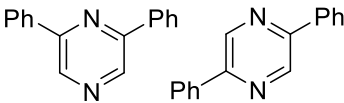




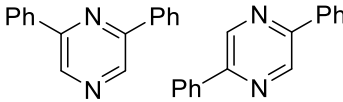
**Figure S15.** <sup>1</sup>H NMR of didodecanepyrazine



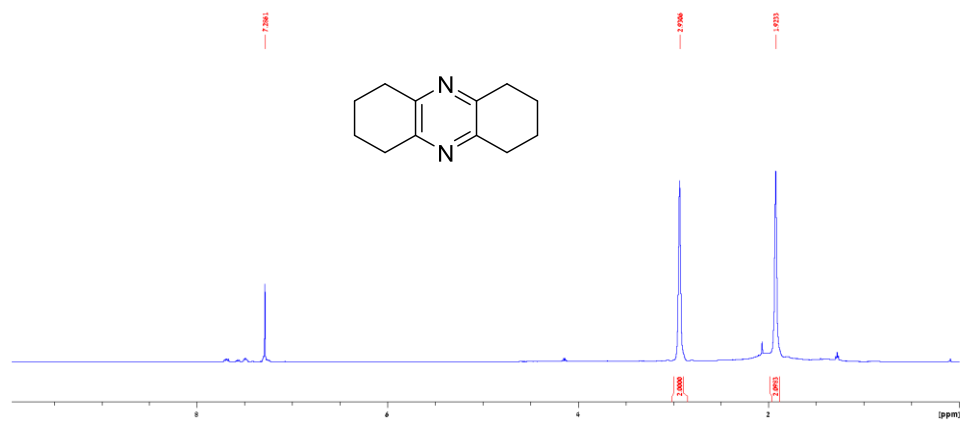
**Figure S16.** <sup>13</sup>C{<sup>1</sup>H} NMR of didodecanepyrazine



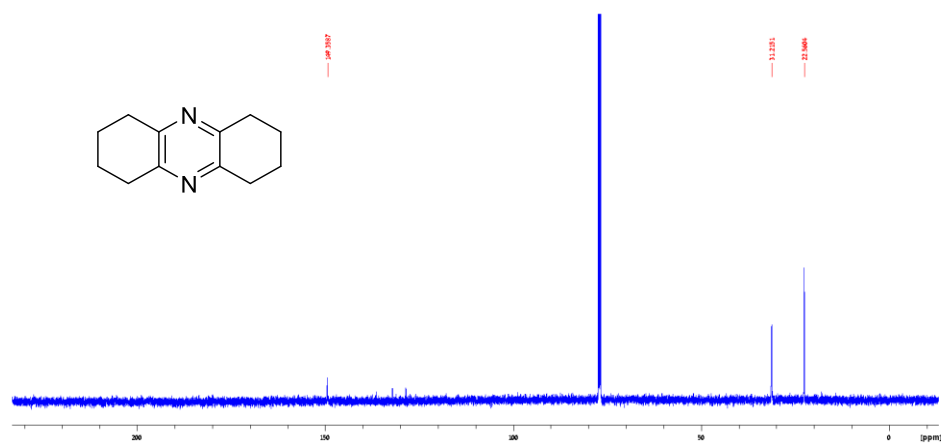
**Figure S17.**  $^1\text{H}$  NMR of diphenylpyrazine



**Figure S18.**  $^{13}\text{C}\{^1\text{H}\}$  NMR of diphenylpyrazine

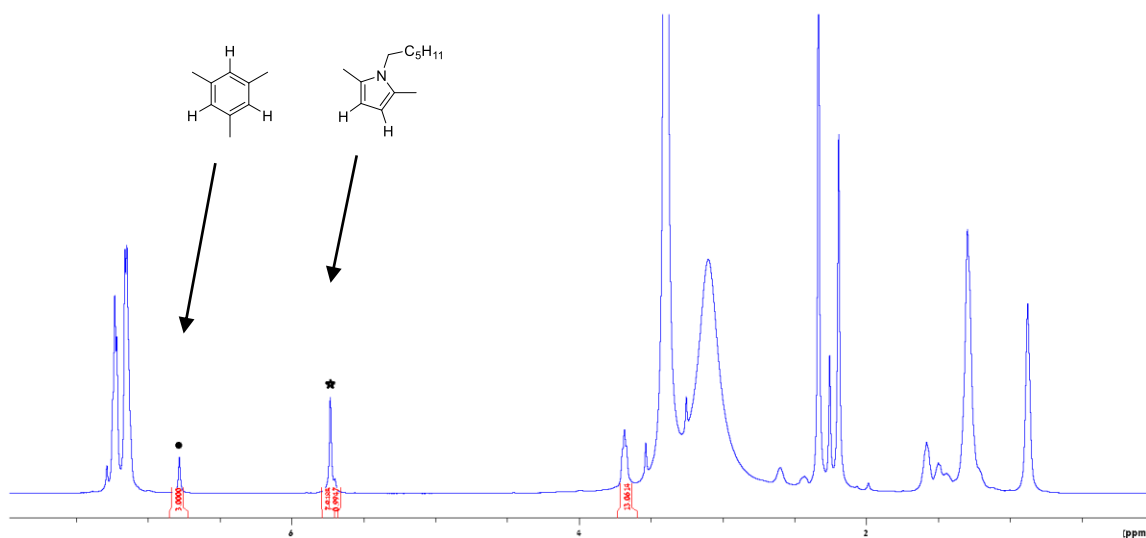


**Figure S19.** <sup>1</sup>H NMR of 1,2,3,4,6,7,8,9-octahydrophenazine

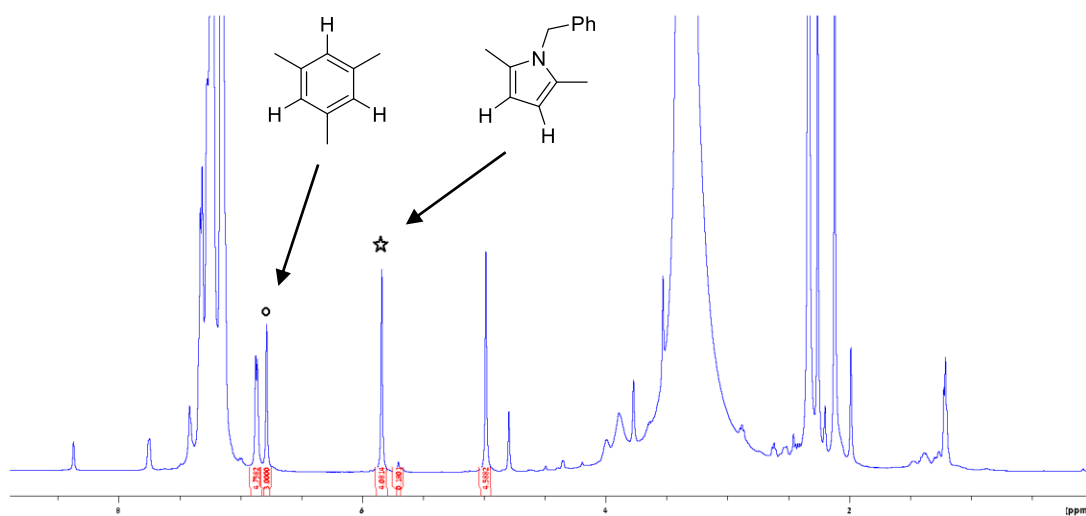


**Figure S20.** <sup>13</sup>C{<sup>1</sup>H} NMR of 1,2,3,4,6,7,8,9-octahydrophenazine

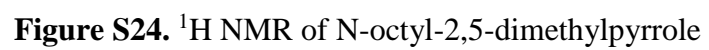
**13.  $^1\text{H}$  NMR spectra of synthesised pyrroles with mesitylene as internal standard:**



**Figure S21.**  $^1\text{H}$  NMR of N-hexyl-2,5-dimethylpyrrole

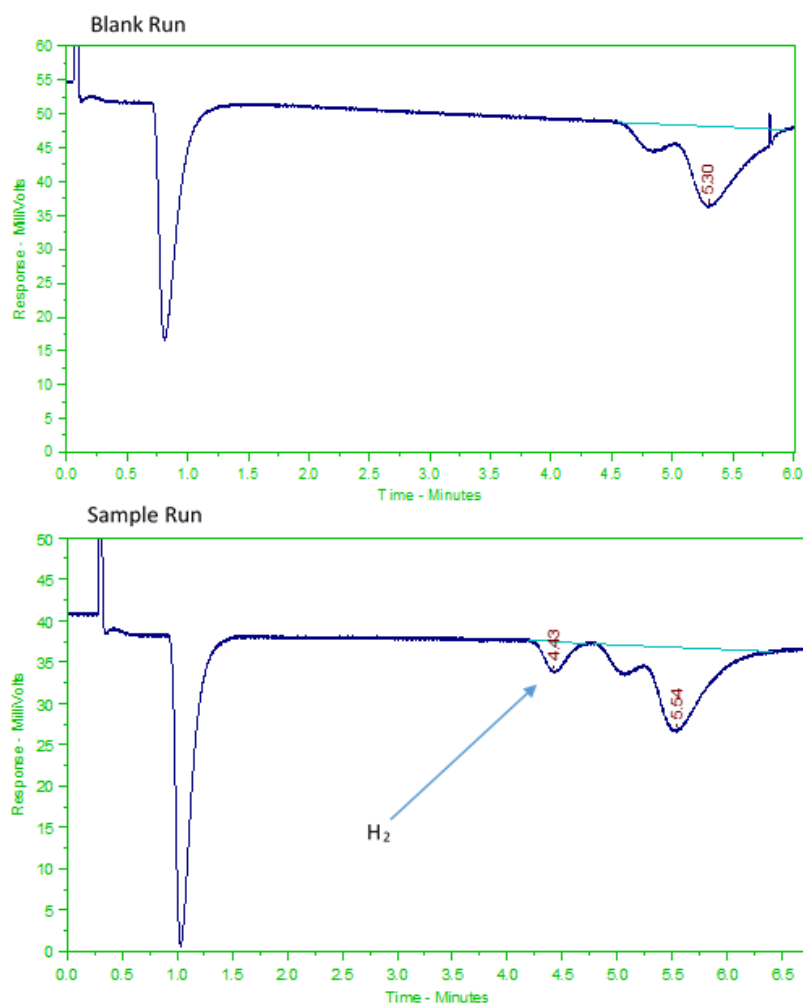


**Figure S22.**  $^1\text{H}$  NMR of N-benzyl-2,5-dimethylpyrrole



#### 14. Procedure for the detection of H<sub>2</sub>:

To a solution of 0.01 mmol catalyst **1** in 0.5 mL dry of toluene in a 100 ml Fisher Porter tube were added 1 mmol of 2,5-hexanediol and 2 mmol of 1-hexanol under N<sub>2</sub> atmosphere. The tube was closed and was taken out of the box, purged with 2 bar of ammonia 3 times and finally pressurized with 7 bar of ammonia. The reaction mixture was stirred at 150°C for 24h and then cooled down to room temperature, followed by further cooling with liq. N<sub>2</sub> to freeze the reaction mixture including gaseous ammonia. The remaining gas mixture was injected into a GC instrument equipped with a thermal conductivity detector, showing formation of H<sub>2</sub>.



**Figure S25.** Thermal conductivity detector GC spectrum for the gas phase analysis after the pyrrole formation reaction

## 15. REFERENCES

- (1) Gunanathan, C.; Milstein, D. Selective Synthesis of Primary Amines Directly from Alcohols and Ammonia. *Angew. Chem. Int. Ed.* **2008**, *47*, 8661-8664.
- (2) Gellrich, U.; Khusnutdinova, J. R.; Leitus, G. M.; Milstein, D. Mechanistic Investigations of the Catalytic Formation of Lactams from Amines and Water with Liberation of H<sub>2</sub>. *J. Am. Chem. Soc.*, **2015**, *137*, 4851–4859.